PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in and relating to Processes of Hydrating Granular Alkaline-earth Metal Oxides

We, SOCIETE D'ELECTRO-CHIMIE, D'ELECTRO-METALLURGIE ET DES ACIERIES ELECTRIQUES D'UGINE, a French Body Corporate, of 10 rue du General Foy, Paris VIIIe, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in processes of hydrating granular alkaline-earth metal oxides.

It is known that the oxides of the common alkaline-earth metals (calcium, barium, strontium, magnesium) can be obtained in granular form, for example by calcination of the carbonates in rocks or crystals previously crushed, but the hydration of these oxides by the known methods is accompanied with such a swelling that it may destroy the cohension and end at the production of pulverulent hydroxides, with the result that the uses for which the hydrated oxides can be employed are limited.

It has now been ascertained that if the temperature of hydration is homogeneous throughout the reacting mass and high enough and the reaction sufficiently slow, the resultant crystalline system of the product, for example of $Ca(OH)_2$, may progressively be formed from the original crystalline system in a continuous manner without provoking the mechanical destruction of the particles.

According to the present invention a process of hydrating granular oxides of alkaline-earth metals comprises contacting the said oxides with a gaseous medium containing water vapour but not saturated therewith, the temperature being maintained homogeneous throughout the reacting mass and controlling the reaction temperature and the concentration of water vapour to promote the formation of hydroxides at a rate such that the said oxides are converted to the corresponding hydroxides without disintegration of the crystal structure of the oxides, the granulation of the starting material being substantially preserved thereby.

Preferably the total amount of water required to react completely with a given mass of oxide is controlled and distributed instantaneously and uniformly throughout the mass of the particles, in order to avoid any possible reaction of the particles with local and transient concentrations of water which are too high to permit the organisation of the molecular of the hydroxide instantaneously produced into the pre-existing crystalline structure.

These conditions of homogeneous temperature and simultaneous reaction in the total mass can be realised by maintaining the mass of particles in a fluidised state by means of a gaseous current with a rate of flow adjusted to the granulation characteristics of the material, and saturated with water by adjustment of the temperature of the current to give a water vapour pressure equal to the water vapour pressure experimentally determined for each stage of the hydration reaction. The water vapour pressure in the gaseous medium is preferably in the range of about 60 to 100 mm of Hg. The total gaseous flux is heated to a temperature sufficient to ensure that it is not saturated with water at any point, in order to prevent any possibility of condensation.

It is possible that the employed gas be air, or a gas inert to the treated oxides.

The hydration of the alkaline-earth oxides does not proceed directly in the single stage represented by the equation:—

$$MO + H_2O = M(OH)_2$$

but by a certain number of intermediary stages which are exothermic to different extents. The water vapour pressure in the fluidizing gas (the flow of which is, as said above, adjusted to the granulation of the

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material) and the reaction temperature resulting at each stage of the hydration are therefore different and their optimum values have to be determined experimentally for each particular case according to the nature of the material which determines the number of reaction stages and the degree to which each is exothermic to its granulation (which determines the flow of the fluidizing gas), to the depth of the fluidised bed (the water content of the fluidizing gas is proportional to the reactional mass), and to the size and degree of heat insulation of the reactor (which determines the thermal loss per unit of mass treated per unit of time).

The applied data concerning the number of reaction stages, the duration of each, the required fluidizing gas input, the water vapour pressure of the fluidizing gas and the corresponding reaction temperatures can be conveniently obtained by laboratory methods, one embodiment of which will now be described by way of example with reference to the accompanying drawings, in which:—

Figure 1 is a diagrammatic representation of a testing apparatus;

Figure 2 is a pair of graphs of the process described in Example I herein; and

Figure 3 is a diagram, similar to the graphs of Figure 2, of the process described in Example II herein.

The drawings with the accompanying description give sufficient information for one skilled in the art to carry out the process herein described on a commercial scale.

Referring to Figure 1, the testing apparatus, gas G under pressure is introduced into a saturator S through a flow meter D capable of determining and adjusting the gas flow according to the granulation of the material to be examined. The saturator S comprises a bubble tube B immersed in water in a flask F closed by a cork and itself immersed in a water bath, the temperature of which can be adjusted so that the gas will entrain water vapour generated in the flask and carry it through a pipe C. The temperature of the space above the water in the flask is measured by a thermometer *t*1 extending through a hole in the cork.

A superheater R is provided having a portion of the pipe C immersed in a heated liquid, for example boiling water, and leading from a point in the flask F above the water therein. The pipe C leads into the base of a reaction tube I, which for example is 30 mm. in diameter and 250 mm. high, containing the oxide P to be hydrated, which tube is also immersed in the liquid in the superheater, this liquid being either boiling water or another liquid, with a boiling point different from that of water, which may be boiling. The tube I is transparent so that the operation can be observed and is provided in its lower portion with a porous plug *p* on which the oxide P is supported. A thermometer *t*2 with its bulb thrust into the oxide mass for reading the temperature of the oxide mass during the successive phases of the hydrating process is provided. The tube I can be separated from the remainder of the apparatus to enable weighings to be made periodically whereby the physical state, particularly the cohesion, of the material to be hydrated, can be followed. By this means the number of phases of the hydration and the duration of each phase can be determined in terms of the operating condition, i.e. the fluidizing gas output, the steam pressure and the reaction temperature.

The following examples, carried out in the aforesaid apparatus, will now be described to make clear the process of the invention.

EXAMPLE I

Hydration of lime: CaO

Calcite crystals, crushed and sifted to a grain size of 100—300 microns, were calcined at 1000° C.

The calcined product, CaO, was placed in the tube I to a static height of 60 mm. The tube was weighed, and then immersed in boiling water. The flow of the fluidizing gas, in the present example air, was then established through the cold saturator S, and then progressively adjusted till the mass was completely fluidized (grains moving along the walls). The fluidizing speed was, at that time, 25 mm/sec. (counted on cold air and on the full section of the tube).

Then the temperature of the saturator was progressively increased. At the same time, the temperature of the fluidized bed was allowed to increase to 120—125° C., which corresponded to a temperature of the saturator of 41—42° (for a water vapour pressure of about 60 mm. of Hg. This saturating temperature was maintained up to the end of the process.

After 20 minutes stabilization, the fluidized bed temperature fell suddenly, and then it stabilized again at 117°. The weighings then indicated that the fall in temperature had started for a weight corresponding to CaO 1/3 H_2O and that the end of the stabilization corresponded to CaO 1/2 H_2O after 32 minutes.

The hydration was carried out, still under 60 mm. of Hg. water vapour pressure. The temperature dropped again, and again became steady at 115°. That level disappeared after 45 minutes; the weight of the material then corresponded to CaO 2/3 H_2O.

After 68 minutes at that level, the temperature was 111° and the weight corresponded to CaO 5/6 H_2O. From this point, the fluidized bed temperature dropped progressively and reached 100° after 105 minutes. The weight then corresponded to $Ca(OH)_2$.

There was observed an increase in volume

of the CaO grains particularly between the stages corresponding to the compositions CaO 1/3 H_2O and CaO 1/2 H_2O. It represented 51% of the initial volume, that is about 13% of the diameter of the individual grains.

The cohesiveness of the product obtained was such that the amount of time material resulting from friction between the oxide grains which was carried off by the fluidizing gas during 105 minutes' fluidization was negligeable.

Diagram I of Figure 2, on which the operation times in minutes are stated in abscissae and the temperatures (in degrees centigrade) in ordinates, represents the whole of the process. The compositions CaO n H_2O are indicated on the corresponding points of the diagram.

Under 100 mm. of Hg. water vapour pressure the complete hydration was obtained within 85 minutes. The temperature evolution was, in that case, much more simple. There was a fall of the temperature when the composition CaO 1/2 H_2O was obtained. It was followed by a progressive cooling up to the composition $Ca(OH)_2$. The increase in volume of the CaO grains was noticeably greater, the times carried off more than in the previous operation. The amount of material carried off by the fluidizing gas was 2.5%.

Diagram 2 of Figure 2 represents the whole of the said second process.

Under 200 mm. of Hg. water vapour pressure the temperature did not remain steady for any part of the process. But, in that case the increase in volume was much greater and the loss by entrainment considerable.

EXAMPLE II

Hydration of calcined dolomite CaO+MgO

A microcrystalline dolomite from La Barasse, at Marseille, crushed in polycrystalline conglomerates of 100—280 microns particle size, was calcined at 1000° C.

A sample of this calcined dolomite was kept fluidized, in a tube immersed in boiling water, by air humidified at 60 mm. of Hg. water vapour pressure.

The laboratory trials showed that:—

(a) the hydration of CaO and of MgO were successively carried out.

(b) the selective CaO hydration seemed to have been made in three phases, the second of which, around CaO 1/2 H_2O, was the most exothermic and was accompanied by an almost total swelling.

(c) at a low water vapour pressure (60 mm. of Hg.) the two first phases succeeded one another without any notable change in the observed temperatures.

(d) the complete hydration of lime in the dolomite is different from that of pure lime and requires, in order to be effected in a reasonable period, a water vapour pressure of about 250 mm. of Hg. which corresponds to a saturator temperature of 72°.

(e) the hydration of MgO, after the complete transformation of CaO into $Ca(OH)_2$ started at water vapour pressure of 300 mm. of Hg. It was markedly exothermic at a water vapour pressure of 400 mm. of Hg.

(f) the total transformation into $Mg(OH_2)$ required a water vapour pressure of about 600 mm. of Hg.

These test data have led to the following working method:—

A dolomite sample, of 100—280 microns particle size was fluidized by a hot air current humidified at 60 mm. of Hg. water vapour pressure.

At first, the exothermic nature of the hydration maintained the temperature of the fluidized bed at 107° for about one hour and then, still at 60 mm. of Hg. water vapour pressure, the fluidized bed temperautre dropped progressively to 101°. That operation lasted 2 hours.

Then the water vapour pressure was increased progressively for a period of 2 hours, to a value of 600 mm. of Hg. The commencement of hydration of MgO was indicated by an increase in the fluidized bed temperature to 103°.

The 600 mm. of Hg. water vapour pressure was then maintained for 30 minutes so as to ensure complete hydration. The increase in volume was finally about 65%, that is 18% in grain diameter. The cohesiveness of the slaked dolomite grains was so good that the entrainment losses from the fluidized bed were about 1.5 to 2.5% after 5-1/2 hours.

The diagrams of Figure 3 (on which the operating hour durations are shown in abscissae, the centigrade temperatures in ordinates and the mercury millimeter water vapour pressures also in ordinates at the lower part of the figure) represent the whole of the said third process.

WHAT WE CLAIM IS:—

1. A process for the hydration of granular alkaline earth oxides which comprises contacting the said oxides with a gaseous medium containing water vapour, but not saturated therewith, the temperature being maintained homogeneous throughout the reacting mass, and controlling the reaction temperature and the concentration of water vapour to promote the formation of hyroxides at a rate such that the said oxides are converted to the corresponding hydroxides without disintegration of the crystal structure of the oxides, the granulation of the starting material being substantially preserved thereby.

2. A process according to Claim 1, wherein the contacting is effected by fluidising a bed of the granular alkaline earth oxide with a current of gas containing water vapour together with air or a gas inert to the treated oxides.

3. A process according to Claim 1 or Claim 2 wherein the water vapour pressure in the gaseous medium is in the range of about 60 to 100 mm. of Hg.

4. A process according to Claim 1 wherein the alkaline earth oxide is calcined dolomite and wherein a moist heated gas in which the water vapour pressure is about 60 mm of Hg is employed during a first part of the process while CaO is being hydrated, and thereafter a higher water vapour pressure of about 600 mm. of Hg. is employed to hydrate the MgO.

5. A process of hydrating granular oxides of alkaline earth metals substantially as herein described.

6. A process of hydrating granular oxides of alkaline earth metals substantially as herein described in Example I or Example II.

7. Hydrated oxides of an alkaline earth metal produced by the process according to any one of Claims 1 to 6.

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3 SHEETS

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SHEET 1

FIG. 1.

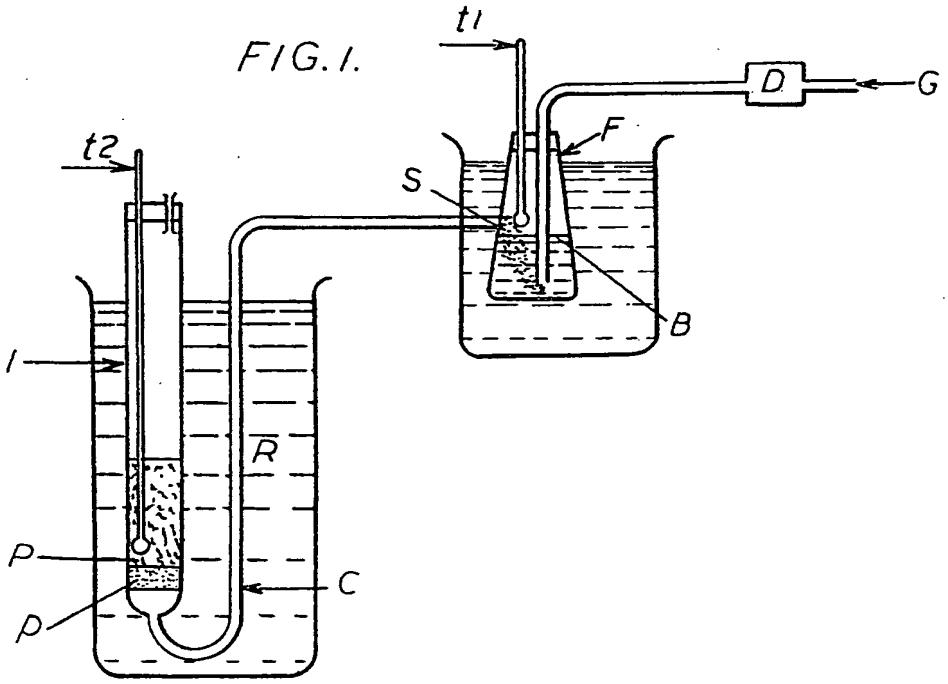
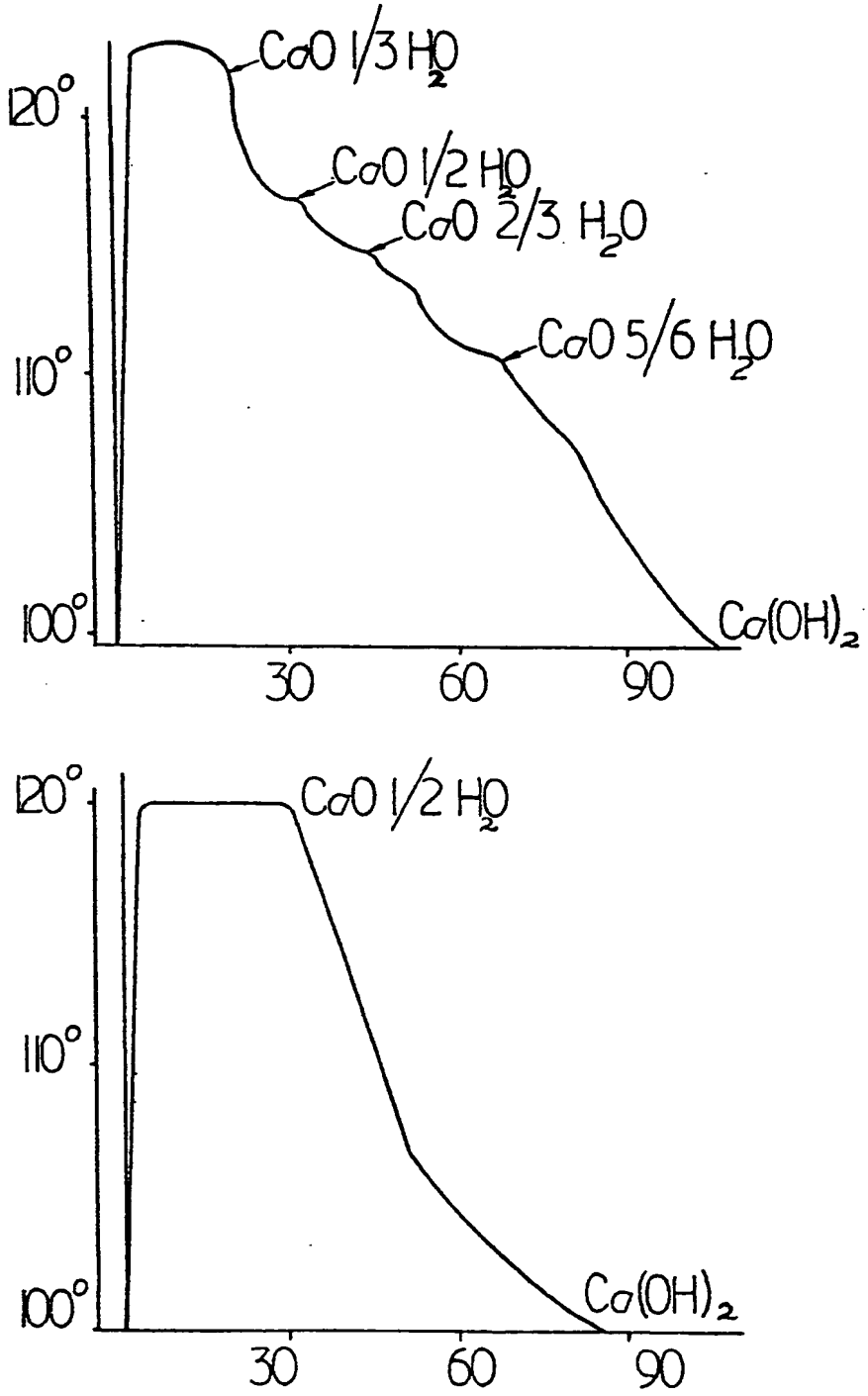


FIG. 2.


120°
110°
100°
CoO 1/3 H2O
CoO 1/2 H2O
CoO 2/3 H2O
CoO 5/6 H2O
Co(OH)2
30
60
90
120°
110°
100°
CoO 1/2 H2O
Co(OH)2
30
60
90

881,813 COMPLETE SPECIFICATION
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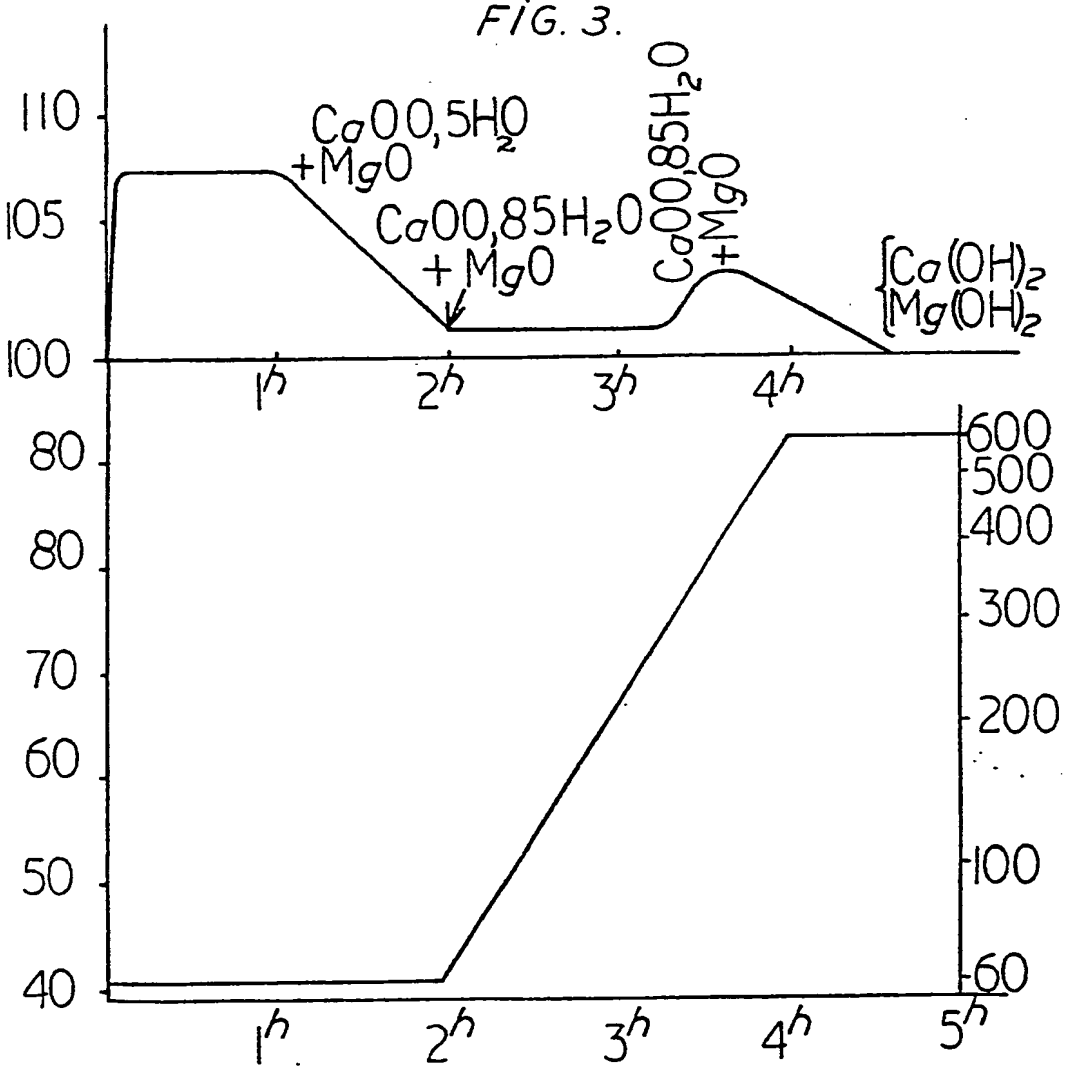
SHEETS 2 & 3

FIG. 3.



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SHEETS 2 & 3

FIG. 2.

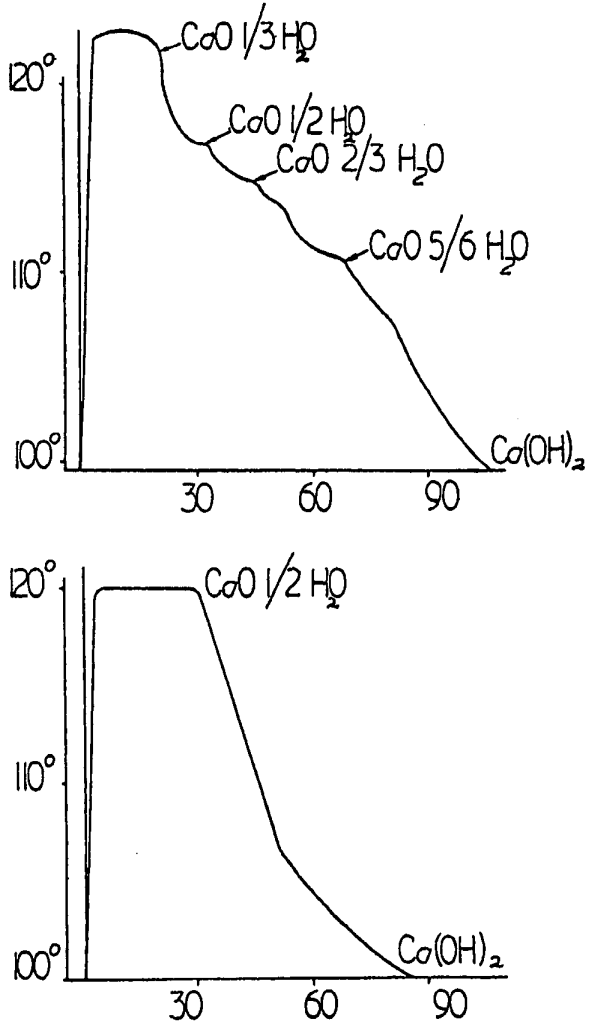
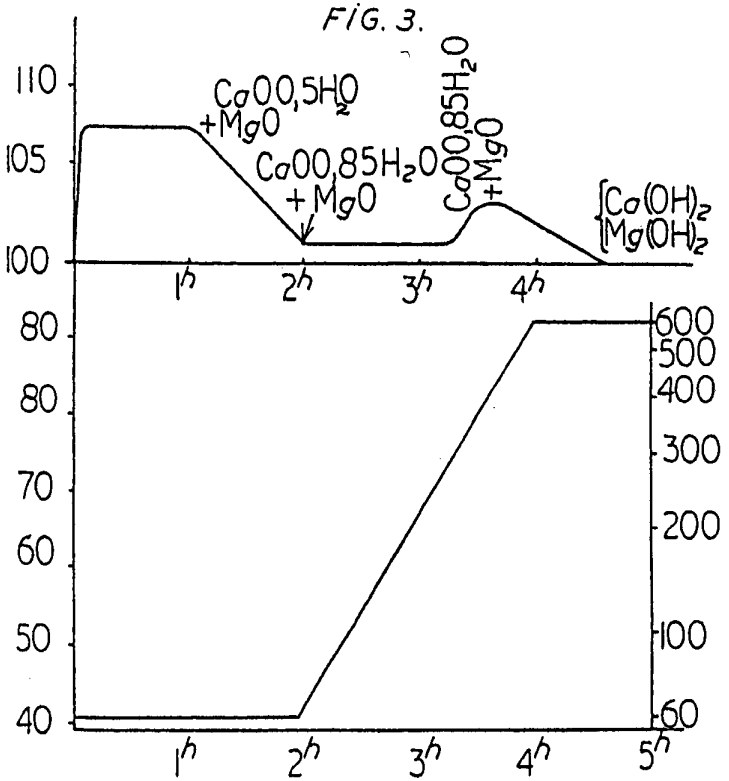


FIG. 3.



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